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(54) PLANOGRAPHIC PRINTING INKS AND PROCESS FOR MAKING AND USING SAME

(71) I, RUSH VIVIAN BLAIR, a Citizen of the United States of America, of 103 West Fourth Street, Peoria, State of Illinois, United States of America, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a printing ink emulsion for use in planographic or lithographic printing and to a lithographic printing process.

The printing ink emulsion may be used in planographic or lithographic printing processes and substantially eliminates the necessity of separate and repeated dampening of the plate between copies.

The present discovery relates to the printing art and in particular, to the field pertaining to planographic or lithographic printing. This type of printing has in recent years become one of the most widely used and, accordingly, much research has been devoted to this area in order to develop new and more efficient materials and processes. Lithographic printing generally entails the use of a planographic printing surface or plate which has areas possessing a distinct selectivity to various substances.

Basically the planographic or lithographic plate is prepared by producing on the surface thereof ink receptive and water receptive areas, the latter being ink repellent areas. When the plate is contacted with an aqueous liquid, the aqueous liquid is adsorbed to the water receptive areas and then when the ink is applied the ink is selectively adsorbed by the ink receptive surface of the plate and accordingly rejected by the ink repellent areas. In the case of indirect or offset lithography the plate, bearing the ink in only those selective areas, is contacted with the printing blanket. The image by means of the ink is transferred to the blanket which in turn transfers the image to the sheet of paper or surface upon which the image is desired. However, in the case of direct lithography, the ink bearing plate is contacted directly with the sheet of paper or surface.

The various processes at present in use for preparing printing plates range from lithographic processes, where a design is made on the surface of a material by applying a greasy, water-repellent, ink receptive material such as crayon or lithographic chalk, to photographic processes where light sensitive bi-chromated gums or light sensitive diazo materials are exposed to an image pattern and the exposed materials are treated to obtain ink receptive areas. Any of these plates may be used with the printing ink of this invention.

In situations where many copies are to be made from the original lithographic plate, flexible plates are wrapped around cylinders and an aqueous solution and ink from separate fountains are supplied by rollers. In a typical printing operation, the cylinder bearing the lithographic plate having ink receptive and ink repellent areas, is first contacted with a roller wetted by a water or other suitable aqueous solution. The aqueous solution is adsorbed by the hydrophilic surfaces but repelled by the ink receptive surfaces. The plate is then contacted with a roller wetted with an oil and the ink is adsorbed by the ink receptive surfaces and rejected in turn by the initial treatment with the aqueous solution. The plate is then contacted with a printing blanket to which the ink is transferred from the blanket to the sheet and the entire process is repeated to obtain the individual sheets bearing the design. This process requires the sequential application of water and ink each time a print is made, and this repeated operation decreases the useful life of the plate. Troubles are also encountered through partial comingling or emulsification of the oil and water on the plate.

One of the proposed methods for overcom-

ing some of the defects of the described process has been the use of water-in-oil emulsion inks. However, the emulsion inks heretofore suggested for use possessed drawbacks which have not made their use particularly feasible. Some of the inks previously proposed did not have the capacity to remain in an emulsive state, that is, these inks have a tendency to demulsify or break in the ink fountain or even during storage. Others do not provide satisfactory prints, particularly where a great number of copies are to be produced. In order to be effective for the purpose, the inclusion of the aqueous dispersed phase in the oily printing ink must not change significantly those physical characteristics of the ink which are requisite to the satisfactory fulfillment of its function as a printing means. When an ink emulsion demulsifies in the ink fountain or does not properly separate or break upon application to the printing surface, the printed image is dull, less intense, and spotted or stipplied. The non-image area is sometimes toned or discoloured.

The present invention is directed to polyhydric alcohol-in-oil emulsion inks, their preparation and use, and in particular to substantially anhydrous emulsion inks which (1) possess the requisite balance of stability for storage and use; (2) permit the obtention of repeated numbers of printed images which do not possess the attendant disadvantages of the prior art water-in-oil emulsion inks; and (3) eliminate the necessity of dampening the lithoplate previous to each application of the emulsion ink during successive printings.

According to the present invention, there is provided a polyhydric alcohol-in-oil ink emulsion for lithographic or planographic printing containing less than 5% by weight water, comprising: (a) an oily ink external phase comprising an oil-wettable ink pigment dispersed in an oily vehicle; and (b) a substantially anhydrous, non-pigmented, polyhydric alcohol internal phase having surface tension properties which facilitate the preferential wetting of the non-image area of a printing plate by said internal phase when the emulsion ink is applied to the plate, the polyhydric alcohol internal phase comprising at least two polyhydric alcohols having from 2 to 5 carbon atoms.

The internal phase preferably contains one or more surfactants which possess the solubilities and surface activities to (a) promote the preferential wetting of the non-image areas of a conventional lithoplate by the polyhydric alcohol, (b) where necessary, maintain the emulsive relationship between the respective phases in the ink fountain while permitting the necessary separation of the phases on the plate, and (c) act as a lubricant between the phases. In general, a surfactant system suitable for purposes of the invention will have a hydrophile-lipophile balance value in the range of from about 12 to 30, but the surfactants must additionally be selected to provide for the preferential wetting of the non-image areas of the lithoplate with the polyhydric alcohol, where necessary, to maintain the desired stability of the emulsion, and desirably to provide lubrication between the phases.

The inks are prepared by mixing the polyhydric alcohols containing the selected surfactant or surfactants with the oily ink dispersion until a substantially homogeneous emulsion is obtained. The use of oil-wettable pigments insures the pigment remains in the external oil phase and does not transfer to the non-pigmented internal polyhydric alcohol phase. The resulting emulsion is allowed to age for a short period of time and then remixed. The use of the emulsion inks of the present invention in lithographic processes eliminates the need for repeated dampening of the lithoplates as a separate step during the printing operation. The polyhydric alcohols preferentially seek out and wet the non-image areas of the plate and repel the oily ink phase. Water is not necessary and may be eliminated entirely.

The oil phase of the emulsion is composed of a suitable oily ink vehicle, including those oils and varnishes which are generally used in printing inks, having dispersed therein a printing ink pigment. The word "oil" as used herein is intended to include all such vehicles. A wide range of printing ink vehicles are known to the art, including hydrocarbonaceous oils such as mineral oil and seal oil, which usually contain predominantly aliphatic components but which may also contain some aromatics, drying oils such as linseed oil, tung oil, other unsaturated oils of either natural or synthetic origin, and mixtures thereof, and varnishes containing either natural or synthetic resins in suitable oily solvent systems. Any of these known vehicles containing pigment dispersed therein may be used as the oily ink phase of the polyhydric alcohol-in-oil emulsion of the invention. While the invention is not limited thereto, varnishes containing long flow isophthalic alkyd resins chlorinated rubber resins or cyclized rubber resins in the proper solvents, as known to the trade, provide very satisfactory vehicles which with added pigment comprise the oil phase of the present composition.

The isophthalic alkyd resins which may be used in the oil phase function not only as an oil but also act to bind the drying oil or varnish pigment dispersion to the surface to which the image is transferred. The use of chlorinated rubber and cyclized rubber resin oils have proved to be very advantageous since these oils permit the obtention of more stable and more uniform emulsions. The selection of surfactant becomes more flexible when the cyclized rubber oils are used since the emul-

sion may be sufficiently stable without dependence upon added surfactant. However, the invention in its broad aspects is not limited to these oils.

Carbon black is the commonly used pigment but it has been found that various coloured inorganic pigments such as the metal oxides, for example, iron oxide, can be used depending, of course, upon the colour desired. Organic pigments such as benzidine yellow, benzidine orange, phthalocyanine blue, phthalocyanine green and Sherman Williams Brilliant toning Red B can also be used. In fact, any coloured pigment which is preferentially wet by the oil phase can be used and will function both as an emulsifier and colouring agent. In addition, the oil phase may contain minor amounts of known additives, such as, agents which prevent the formation of skin upon exposure of the oil phase to air, and agents such as stearic acid which improve the ability of the oil phase to cover the ink receptive area of the printing plate. These additional ingredients and their respective functions are well known to the artisan and can be varied or even eliminated as the situation demands. The oil phase may constitute from 50% to 85% by weight of the total emulsion weight and preferably constitutes from 58% to 84% by weight.

The internal phase is composed primarily of the polyhydric alcohols, particularly mixtures of trihydroxy and dihydroxy alcohols, in which the surfactant or mixture of surfactants has been dissolved or dispersed, where necessary.

The alcohols which have been found to yield particularly good quality inks are glycerine and ethylene glycol, but other polyhydric alcohols containing from 2 to 5 carbon atoms and having generally the same properties may be used. Representative of such other alcohols are 1,3-butanediol, 1,4-butanediol, 1,5-pentane diol, and 2,2′-oxydiethanol. Two or more of the alcohols may be used in proportions selected to impart desirable viscosity and flow properties to the polyhydric alcohol phase of the emulsion. This phase constitutes from 15% to 50%, and preferably from 16% to 42%, by weight of the total weight of the emulsion. These percentages include the content of the surfactant or surfactants which when required usually represents from 0.2% to 3% by weight of the total emulsion weight of more specifically represents from 3% to 6.8% by weight of the total weight of the internal phase. No water is necessary or desirable in the composition although a small amount of water, such as may be included with surfactant solutions, or absorbed from the atmosphere may be tolerated. In general, the amount of water, if present at all, is less than 5%. The expression "substantially anhydrous" as used herein does not include such minor amount of water.

The surfactant or surfactants of the system may be those which possess a hydrophile-lipophile balance (referred to as HLB) which is capable (a) of maintaining the polyhydric alcohol-in-oil emulsive relationship, (b) of providing the necessary lubrication between the two phases, and (c) of permitting the preferential wetting of the non-image areas of a lithoplate with the polyhydric alcohol, three properties which are imperative if an emulsion ink is to perform as necessary. The HLB of an emulsifier is an expression of its hydrophile-lipophile balance, i.e., the balance of the size and strength of the hydrophilic (water-loving or polar) groups and the lipophilic (oil-loving or non-polar) groups of the emulsifier.

A single surfactant may act in all three capacities or satisfactory results can be obtained by choosing different surfactants tailored to meet the three objectives above, i.e., a multi-component system with one component serving to lower the surface tension of the polyhydric alcohol, another serving to stabilize the alcohol-in-oil emulsion and still another to serve as a lubricant. In certain instances, the oily phase containing the dispersed pigment may be of such nature that a sufficiently stable emulsion with the polyhydric alcohol is formed without the necessity of incorporating a surfactant in the polyhydric alcohol phase to serve the emulsion stabilizing function. In this instance it is only necessary that a surfactant be selected which is soluble in the polyhydric alcohol phase and which will lower its surface tension and/or serve as a lubricant. Those skilled in the art, guided by the present disclosure, will know how to select surfactants to accomplish the objectives stated. See, for example, the publication of the Atlas Chemical Industries, Inc. entitled "The Atlas HLB System" copyright 1963. The surfactant system of the invention must be at least partially soluble in the polyhydric alcohol, cause the alcohol to preferentially wet the non-image areas of the plate, cause lubrication between the phases and, if necessary, at the same time keep the alcohol emulsified in the oil while the ink is in the fountain.

It is known both theoretically and experimentally, barring other offsetting influences, that the lower surface tension liquids wet metal or other high surface-energy solids more easily. The surface tension values for all liquids are temperature dependent. At room temperature most of the lower molecular weight glycols exceed 35 dynes/cm and those for the organic oils (the basic ink components) are less than 35 dynes/cm. Hence on the absence of any surfactant or other offsetting condition the oil-carbon black dispersion will compete sucessfully for the image and non-image areas of the lithographic plate alike. However, in the presence of a glycol-soluble

surfactant that lowers the glycol surface tension to a value slightly below that of the oil-carbon black phase, it will be the glycol that wets the non-image area and not the oil-carbon black dispersion. It is further observed that if the glycol surface tension is lowered excessively, it will begin to wet even the naturally glycol-repellent image area. An offsetting condition in this invention which aids the non-image area being preferentially wet by the internal phase is that initially the non-image area is wet by a polyhydric alcohol solution with a sponge, cotton pad or cloth. Hence for the oily ink phase to subsequently wet the non-image area, the absorbed layer of polyhydric alcohol must first be removed. But because this polyhydric alcohol layer is continually being replenished via the internal phase during the printing operation and because the polyhydric alcohol phase is bound strongly to the non-image area, it is difficult if not impossible for the oily ink phase to gain access to the non-image area. Hence some formulations do not require the addition of wetting agents.

The experimental effects of surfactants acting as emulsifiers are well known. As noted above, the reason for emulsification of the glycol and oil-carbon black dispersion is to permit the transfer of ink from the ink fountain to the inking rollers and then to the lithographic plate. Where combinations of surfactants for wetting, lubrication and emulsification are employed, any emulsifier that does not interfere with the wetting and lubricating surfactant is permissible.

If the oil phase and the polyhydric alcohol phase are mixed in the presence of a suitable surfactant system when required to accomplish the above, the ink emulsion obtained is not only stable in the ink fountain, but upon use in a lithographic process permits the preferential wetting and provides for good ink distribution on the ink rollers. In addition an adequate number of impressions per plate with each impression exhibiting good intensity and definition and, in general, a fine quality can be obtained. These impressions can be made without the necessity of dampening the lithoplate after each printing and before the application of the ink.

In using the present emulsion inks the plate may be preliminarily contacted before the first printing with a liquid which will preferentially wet the non-image areas and attract the internal phase of the ink. This liquid need not contain water, although aqueous solutions, such as aqueous glycerine solutions, can be used at this stage. A suitable pre-dampening liquid is a polyhydric alcohol containing an agent which will lower its surface tension, such as, for example, a liquid identical to the internal phase of the ink emulsion. Glycerine-ethylene glycol solutions which have been acidified, e.g. with oxalic acid are also quite suitable. The plate is contacted with the pretreating solution before the first printing only since the subsequent dapenings are accomplished by the polyhydric alcohols of the ink itself.

Representative surfactants which may be included in the surfactant system are (a) the mono- and di-glycerides of fatty acids such as stearic, palmitic, oleic, lauric acids and mixtures thereof; (b) polyoxyalkylene fatty acid polyolesters such as polyoxyethylene sorbitan monostearate, polyoxyethylene propylene glycol monostearate, polyoxyethylene glycol monolaurate, polyoxyethylene glycol mono-oleate, polyoxyethylene glycol monostearate, polyoxyethylene glyceryl stearate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan trioleate, and polyoxyethylene sorbitan monooleate, which are soluble in the polyhydric alcohol phase; and (c) surfactants of the morpholinium salt type and represented by N-soya-N-ethyl morpholinium ethosulfate, and N-cetyl-N-ethyl morpholinium ethosulfate. Types (a) and (b) are representative of non-ionic surfactants which may be blended together or with other non-ionic or cationic surfactants having a higher HLB value. The type (a) surfactants have a relatively low HLB value and perform the function of stabilizing the polyhydric alcohol-in-oil emulsion. The type (b) non-ionic surfactants are more strongly hydrophilic than type (a), in general are soluble in the polyhydric alcohols and lower their surface tension and promote their wetting of the printing plate. Other surfactants which will perform this function as well as providing lubrication between the phases, and which can be used alone where emulsion stability is not a problem, include certain organo-silicones having combined hydrophobic and hydrophilic action in the same molecule, such as those wherein the molecule contains a silicone portion providing low surface tension and hydrophobic characteristics and a polyoxyalkylene portion, providing hydrophilic action and compatibility with other materials. Such products are described in a Technical Service Bulletin of the Research and Development Department of the Union Carbide Corporation entitled "Union Carbide" L-75, L-76, L-78 and L-79 Organo-silicone Surfactants. Members of type (a) and (b) can be selected in suitable proportions to provide an HLB in the range of 12 to 30. The cationics of type (c), in general, have an HLB in the upper portion of the recited range and possess the necessary wetting and emulsifying properties to be used alone in the emulsion inks of the invention. They can also be used to raise the HLB value of the non-ionics (a) and/or (b) to provide a surfactant system capable of performing the triple function required. It will be understood that the invention is not limited to the use of these recited surfactants but can employ any surfactant system capable

of performing the necessary functions in the polyhydric alcohol-in-oil emulsions.

The amount of surfactant or surfactants added to the emulsion and more specifically, to the polyhydric alcohols depends upon the surfactants selected and the HLB value of the surfactant system as well as on the composition and the relative percentages in the emulsion of the respective phases. The amount of surfactants used can only be generally defined in terms of function, i.e., that which is necessary at the selected HLB within the stated range to (i) maintain the emulsive relationship between the two phases, where necessary, (ii) to accomplish the preferential wetting of the image and non-image areas of a lithoplate, and (iii) to provide lubrication between the phases.

The process of producing the subject polyhydric alcohol-in-oil emulsion ink comprises the steps of initially mixing the alcohols with the surfactant or surfactants. Optionally, a pH control agent may be included to ensure that the ink remains substantially neutral or slightly on the acid side. A small amount of potassium bitartrate or equivalent buffer is suitable for this purpose. After an intimate mixture, or more specifically, a solution or dispersion has been obtained, the oil medium composed of an ink pigment dispersed in an oil generally used for the purpose, is admixed with the polyhydric alcohol solution. The medium is then mixed for a period of time until an emulsion or a completely homogeneous mixture of droplets of the polyhydric alcohol solution dispersed in the external or oil phase is obtained. The emulsion is then allowed to stand at the ambient conditions for a period of time ranging from a few hours to 24 hours and then remixed to ensure that a complete dispersion is attained. The emulsion can be used after cooling; however, it is preferable to allow the emulsion to age for a period of a few days and as long as 30 days. The aging period permits the emulsion to attain a state of thermal equilibrium which in turn enhances the stability characteristics of the emulsion.

As earlier stated, the emulsion inks of the present application contain various ingredients each of which serves a distinct purpose. The pigment oil phase serves to ink the ink receptive surface of the lithopraphic plate while the polyhydric alcohol phase serves to dampen or wet the hydrophilic or water receptive areas in order to insure that these areas do not for one reason or another accept the ink.

The polyhydric alcohol-in-oil emulsion of the invention can be used quite effectively with any of the lithographic direct or offset printing processes which employ conventional printing plates having ink receptive and ink repellent areas. In a representative embodiment, the plate (e.g. a paper direct, photo plate or metal lithographic plate prepared in the usual manner) is installed in a printing apparatus which is conventional in design with the exception that a separate water fountain and plate dampening mechanism for the conventional and sequential dampening of the plate is not necessary. The plate is initially dampened with the pretreating solution which is attractive to the internal phase of the ink as by means of a cloth or sponge and a film of the polyhydric alcohol-in-oil emulsion ink in accordance with the invention is then applied to the dampened plate generally by means of the conventional ink roller. The milling action of the roller in contact with the plate facilitates de-emulsification and separation of the phases of the ink to permit their distribution to the plate areas individually attractive to them. The plate is then contacted with the surface to which the image is to be transferred or to a printing blanket. Where the image is transferred to a blanket the image is then in turn transferred to the surface of the material upon which the image is desired. The process is repeated with the exception that the plate is not dampened before each subsequent application of ink.

The present polyhydric alcohol-in-oil emulsions can be used to produce multi-coloured impressions merely by changing the pigment colour and reprinting upon the same sheets upon which the initial coloured impression was made.

The invention, having thus been generally described, will now be described in detail. However, the detailed descriptions are not to be construed as limiting but rather, are to be considered for illustrative purposes only.

Example 1

To one-half a fluid ounce of a mixture of 2 parts glycerine (7.46 g.) and 3 parts ethylene glycol (9.84 g.) was added one gram of Cream of Tartar (Potassium bitartrate), 0.1 gram of Ottasept (a fungicide which contains as active ingredients p - chloro - m - xylenol and 4 - chloro - 2, 6- xylenol and which is available from Ottawa Chemical Company) and one gram of a surfactant system having an HLB of 16.5 produced by blending the following:

90% Atlas G-1300-Polyoxyethylene glyceride ester having an HLB of 18.1, and

10% Atlas Arlacel No. 186-A mixture of mono- and diglycerides of fatty acids having an HLB of 2.8 and containing a few hundredths of a percent of preservatives. ("ATLAS" and "ALACEL" are Registered Trade Marks).

These materials were thoroughly mixed until a uniform solution was obtained. The polyhydric alcohol base solution thus obtained was added with mixing to 50 grams oil based carbon black ink having the following composition:

41.75 grams of carbon black pigment
198.45 grams of chinawood gel (tung oil)
113.40 grams of a long flow isophthalic alkyd resin
3.0 grams of hydroquinone (an anti-skin agent)

The medium was mixed thoroughly until a completely homogeneous emulsion of the droplets of the polyhydric alcohol phase (internal) dispersed in the oil phase (external) was obtained.

The emulsion was then allowed to stand at ambient conditions for a period of 24 hours to allow settling of any undispersed materials and to allow the emulsion to reach thermal equilibrium since there is a redistribution of heat during mixing. After this, the emulsion was again mixed thoroughly. After the final mix, the emulsion was allowed to age for about 7 days at ambient conditions in a closed container during which substantially complete thermal equilibrium is reached.

Example 2

Example 1 was repeated with the exception that 1 gram of a surface active agent, Atlas No. 263, a 35% aqueous solution of N-cetyl-N-ethyl morpholinium ethosulfate having an HLB of about 30 was substituted for the surfactant i.e. the mixture of 90% Atlas G 1300 and the 10% Atlas Arlacel No. 186.

Example 3

Example 2 was repeated with the exception that only one-quarter of an ounce of the mixture of glycerine and ethylene glycol was used and a cationic surfactant, Atlas G-271 a 35% aqueous solution of N-soya-N-ethyl morphoninium ethosulfate, having an HLB of from about 25 to 30 was used in place of the aqueous solution of N-cetyl-N-ethyl morpholinium ethosulfate used in that Example.

Example 4

Example 3 was repeated with the exception that one-half of a fluid ounce of the glycerine, ethylene glycol solution was used.

Example 5

Example 4 was repeated with the exception that 1.5 grams of the 35% aqueous solution of N-soya-N-ethyl morpholinium ethosulfate (HLB=25—30) was used.

Example 6

To one fluid ounce of a mixture of two parts glycerine (14.92 g.) and 3 parts ethylene glycol (19.68 g.) was added one gram of Cream of Tartar (potassium bitartrate), 0.1 gram of Ottasept (a fungicide which contains as active ingredients p - chloro - m - xylenol and 4 - chloro - 2, 6 - xylenol and which is available from Ottowa Chemical Company) and one gram of a cationic surfactant Atlas G-271 a 35% aqueous solution of N-soya-N-ethyl morpholiniunm ethosulfate, having an HLB of from about 25 to 30.

The resulting admixture was thoroughly mixed until a uniform solution was obtained. The solution thus obtained was added with mixing to 100 grams of chlorinated Latex resin varnish based carbon black ink having the following composition:

150 grams of Pope & Gray Latex varnish No. VZ2361 (chlorinated rubber latex in appropriate hydrocarbon oil solvent)
45 grams carbon black

The medium was mixed thoroughly until a completely homogeneous emulsion of the droplets of the polyhydric alcohol phase (internal) dispersed in the oil phase (external) was obtained.

The emulsion was then allowed to stand at ambient conditions for a period of 24 hours to allow settling of any undispersed materials and to allow the emulsion to reach thermal equilibrium. After this, the emulsion was again mixed thoroughly. After the final mix, the emulsion was allowed to age for about 7 days at ambient conditions in a closed container during which substantially complete thermal equilibrium is reached.

Example 7

Example 1 was repeated with the exception that the pigmented oil contained iron oxide (red-pigment) as the pigment in place of the carbon black.

Example 8

To one and one-half ounces of a mixture of 2 parts glycerine (7.46 g.) and 3 parts ethylene glycol (9.84 g.) was added two grams of Cream of Tartar, 0.1 g. Ottasept and two grams of the surfactant Atlas G-271 which is a 35% aqueous solution of N-soya-N-ethyl morpholinium ethosulfate having an HLB of 25 to 30. The resulting materials were thoroughly mixed until a uniform solution was obtained. The resulting polyhydric alcohol base solution was added with mixing until thoroughly mixed with 100 grams of an oil-based black ink to which 1 gram of magnesium silicate had been added and mixed. The oil based black ink had the following composition:

113.45 g. carbon black pigment
113.45 g. water resistant gloss
226.90 g. long flow isophthalic alkyd resin
3.00 g. hydroquinone

The medium was mixed thoroughly until a completely homogeneous emulsion was

obtained. The emulsion was then allowed to remain at room conditions in a closed container for approximately 24 hours. After this period the emulsion was again thoroughly mixed and then allowed to age for 7 days. After this period the emulsion was examined and found to be stabilized and ready for use.

Example 9

By procedure similar to that of Example 8 an emulsion ink was prepared from the following:

External phase
- 100 grams as follows:
  - 75% LBX 296—25 Varnish (a heavy print varnish containing approximately 73% cyclized rubber dissolved in a paraffinic hydrocarbon solvent having a boiling range of 620—675°F) 25% carbon black

Internal phase
- 2 fluid ozs, as follows:
  - 2 parts glycerine
  - 3 parts ethylene glycol
- 2 grams Atlas G-271 Surfactant
- 2 grams Atlas G-263 Surfactant
- 6 grams Cream of Tartar
- 6 grams gum tragacanth

Example 10

An emulsion ink was prepared according to the following formula:

(a) 100 grams external phase containing 30% by weight of carbon black milled into 70% by weight of a varnish prepared by dissolving 42% by weight of a petrol soluble cyclized rubber resin having a melting range of 125—140° C (capillary method) in 58% by weight of a solvent mixture of aliphatic petroleum oil solvents having boiling ranges within 450 to 700°F of the type used in the preparation of heat set printing inks to which 2.4% by weight, based on the weight of the solvents, or stearic acid has been added;

(b) 2 fluid ounces internal phase consisting of 2 parts by weight of glycerine and 3 parts by weight of ethylene glycol to which 2 grams of a non-ionic organo-silicone surfactant (L-76 Silicone, Union Carbide) for reducing surface tension and for lubrication between the phases has been added.

The components (a) and (b) were thoroughly mixed and allowed to set for approximately 7 days before use. The emulsion was used in lithographic printing as herein described with excellent results.

Example 11

A silicated aluminium plate coated with a diazo material (as for example described in U.S. Patent No. 2,714,066) was exposed through an image pattern and treated in a conventional manner to produce a reproduction of the image defined by ink receptive and ink-repellent (water receptive) areas.

The lithographic plate thereby produced was installed in a conventional lithographic printing apparatus with the water fountain and dampening rollers removed therefrom. The lithoplate was then dampened with aqueous glycerine solution and the dampened plate was then contacted with glycol-in-oil emulsion ink as produced according to Example 1. The ink portion of the ink emulsion was attracted to and covered the ink receptive areas while the polyhydric alcohol phase of the ink emulsion covered the water receptive or ink-repellent areas. The inked plate was then contacted with a printing blanket to which the ink was transferred and the printing blanket was then contacted with a sheet of paper so as to transfer the ink image to the paper. The process was repeated with the exception that the initial dampening step was eliminated and the plate yielded impressions possessing excellent intensity and definition and, in general, good quality. The subsequently obtained impressions made without a separate dampening step were as good in quality as the first impression made after the first and only dampening step of the process. Accordingly, it was evident that the respective phases performed as required.

Example 12

The process of Example 11 was repeated. However, in order to increase the polyhydric alcohol receptive nature of the ink repellent portions of the lithographic plate, the plate was initially treated with an aqueous solution containing a small amount of glycerine and cationic surfactant Atlas G-271. The printing process was then carried out as described in the foregoing example and again impressions of excellent intensity and definition were obtained.

Example 13

The process of Example 11 was repeated using in place of the glycol-in-oil emulsion of Example 1 the emulsion as described in Example 4. More than an acceptable number of impressions were made which exhibited good intensity and excellent definition. The plate upon inspection did not show any signs of deterioration and additional fine quality prints could have been made.

Example 14

The process of Example 11 was repeated using the ink emulsions of each of the Examples 1—10 except that the initial dampening solu-

tion was substantially anhydrous mixture of glycerine and ethylene glycol which had been acidified with oxalic acid. Excellent results were obtained.

Example 15

The process of Example 11 was repeated until a sufficient number of copies were made. The lithoplate was then removed from the printing apparatus and a second plate bearing an image or design which was to be printed on the sheets of copies bearing the initial impressions. The red coloured polyhydric alcohol-in-ink emulsion as described in Example 7 was then substituted for the black ink emulsion and the copies were replaced in the appropriate place in the printing apparatus.

The process was carried out as described in Example 11 and prints were obtained which possessed separate black and red images or designs.

Example 16

An emulsion ink was prepared, as in Example 10, from the following:

		Parts by wt.
1. External phase		
(a) Ink varnish		140
Cyclized natural rubber (Alpex 450J-American Hoechst Corp.)	38.56%	
Low molecular wt. Natural fossil hydrocarbon resin (Parco No. 200—Pan-American Resin and Chemical Co.)	5.8%	
Aliphatic Petroleum Oil Solvents (13.33% Mentor No. 32 oil of Humble Oil Co., 13.34% Magie No. 470 oil and 26.67% of Magie No. 535 oil of Magie Bros, Oil Co.)	53.34%	
Stearic Acid	2.30%	
(b) Carbon Black (Regal SR.—Cabot Corp.)		60
2. Internal Phase		
(a) Glycerol		24
(b) Ethylene Glycol		36
(c) Organo-silicone surfactant (L-76 Silicone—Union Carbide Co.)		4
		264

("PARCO", "MENTOR" and "REGAL" are Registered Trade Marks).

Examples 17—20

Emulsion inks are prepared from the same formulation as in Example 16 except that in lieu of carbon black the pigments are:

Example 17—benzidine orange
Example 18—phthalocyanine blue
Example 19—phthalocyanine green
Example 20—William's Brilliant Toning Red B

Examples 21—25

Emulsion inks were prepared from the same formulation as in Example 16 except that the polyhydric alcohol content of the internal phase was as follows:

	Parts by wt.
Example 21—	
(a) Propylene glycol	20
(b) Ethylene glycol	40
Example 22—	
(a) 1,3-Butanediol	24
(b) Ethylene glycol	36
Example 23—	
(a) 1,4-Butanediol	24
(b) Ethylene glycol	36
Example 24—	
(a) 1,5-Pentanediol	24
(b) Ethylene glycol	36
Example 25—	
(a) 2,2′-Oxydiethanol	40
(b) Ethylene glycol	20

Each of the inks of Examples 16—25 are suitable for the purposes of the present invention. To show the importance of using polyhydric alcohols of 2—5 carbon atoms further ink samples were made up using the same formulation as in Example 16 except that one of the polyhydric alcohols of the internal phase contained more than 5 carbon atoms. The results are shown in the following Table in which Tests 1, 2, 3, 4 and 6 were run on the inks of the foregoing Examples 21 to 25, respectively.

TABLE

Test No.	Internal Phase Mixture	No. of Carbons in Mol.	Results
1	2 Parts Ethylene Glycol	2	satisfactory
	1 Part Propylene Glycol	3	
2	3 Parts Ethylene Glycol	2	satisfactory
	2 Parts 1,3-Butanediol	4	
3	3 Parts Ethylene Glycol	2	good
	2 Parts 1,4-Butanediol	4	
4	3 Parts Ethylene Glycol	2	satisfactory
	2 Parts 1,5-Pentanediol	5	
5	3 Parts Ethylene Glycol	2	poor
	2 Parts 2,5-Hexanediol	6	
6	3 Parts Ethylene Glycol	2	satisfactory
	2 Parts 2,2'-Oxydiethanol	4	
7	3 Parts Ethylene Glycol	2	poor
	2 Parts N-Hexanol	6	
8	3 Parts Ethylene Glycol	2	poor
	2 Parts 2-Methyl-2,4-Pentanediol	6	
9	3 Parts Glycerol	3	poor
	2 Parts 2-Methyl-2,4-Pentanediol	6	

WHAT I CLAIM IS:—

1. A polyhydric alcohol-in-oil ink emulsion for lithographic or planographic printing containing less than 5% by weight water, comprising: (a) an oily ink external phase comprising an oil-wettable ink pigment dispersed in an oily vehicle; and (b) a substantially anhydrous, non-pigmented, polyhydric alcohol internal phase having surface tension properties which facilitate the preferential wetting of the non-image area of a printing plate by said internal phase when the emulsion ink is applied to the plate, the polyhydric alcohol internal phase comprising at least two polyhydric alcohols having from 2 to 5 carbon atoms.

2. An ink emulsion as claimed in claim 1 wherein the polyhydric alcohol internal phase is a mixture of at least one dihydroxy alcohol having 2 to 5 carbon atoms and glycerine.

3. An ink emulsion as claimed in claim 2 wherein the mixture comprises ethylene glycol and glycerine.

4. An ink emulsion as claimed in any one of claims 1 to 3 wherein the external phase constitutes from 50% to 85% by weight of the total emulsion and the internal phase constitutes 15% to 50% by weight of the total emulsion.

5. An ink emulsion as claimed in any one of claims 1 to 3 wherein the external phase constitutes 58 to 84% by weight of the total emulsion and the internal phase constitutes 16 to 42% by weight of the total emulsion.

6. An ink emulsion as claimed in any one of the preceding claims wherein the polyhydric alcohol internal phase contains from 3 to 6.8% by weight based on the weight of said internal phase at least one surfactant having hydrophile-lipophile balance of from 12 to 30 which lowers the surface tension of the polyhydric alcohol, said surfactant being selected from (a) mono- and di-glycerides of fatty acids (b) polyoxyalkylene fatty acid polyol esters (c) morpholinium quaternary ammonium salts (d) organo-silicones, and (e) mixtures thereof.

7. An emulsion as claimed in claim 5 wherein the surfactant comprises a mixture of a surfactant (a) with a surfactant (b) or (c) having a higher HLB value than (a).

8. An emulsion as claimed in claim 5 wherein the surfactant material comprises a morpholinium quaternary ammonium salt.

9. An emulsion as claimed in claim 7 wherein the morpholinium quaternary ammonium salt is N - cetyl - N - ethyl - morpholinium ethosulfate or N - soya - N - ethyl - morpholinium ethosulfate.

10. An emulsion as claimed in claim 6 or claim 7 wherein the surfactant comprises a mixture of mono- or di-glyceride of a fatty acid and a polyoxyethylene glyceride ester.

11. An emulsion as claimed in any one of the preceding claims wherein the pigment of the external phase is carbon black and the vehicle of the external phase is an ink oil selected from synthetic oils, varnishes, linseed oil, tung oil and mixtures thereof.

12. An emulsion as claimed in any one of the preceding claims wherein the ink vehicle is a printing ink varnish comprising a cyclized rubber resin dissolved in a hydrocarbon oil solvent.

13. An emulsion as claimed in any one of the preceding claims wherein the ink vehicle is a printing ink varnish containing a chlorinated rubber resin.

14. A polyhydric alcohol-in-oil printing ink emulsion for lithographic or planographic printing containing less than 5% by weight water, comprising: (a) from 50 to 85% by weight of an external phase comprising an ink pigment dispersed in a printing ink varnish

containing a cyclized rubber resin dissolved in a hydrocarbon oil solvent; and (b) from 15 to 50% by weight of a substantially anhydrous, non-pigmented internal phase comprising a mixture of glycerine and ethylene glycol containing at least one surfactant in an amount sufficient to lower the surface tension of the mixture of alcohol so as to promote preferential wetting of the non-image areas of the printing plate when the emulsion ink is applied to the plate, and serve as a lubricant between the internal and external phases of the emulsion.

15. An emulsion as claimed in claim 13 wherein the surfactant of the internal phase is an organo-silicone.

16. An emulsion as claimed in claim 13 or claim 14 wherein the external phase includes a low-molecular weight natural fossil hydrocarbon resin.

17. A process of lithographic printing which comprises: (a) contacting a lithographic printing plate possessing an image defined by ink receptive and ink-repellent areas with an emulsion containing less than 5% water and comprising 50 to 85% by weight of an oily ink external phase comprising an oil-wettable ink pigment dispersed in an oily ink vehicle and from 15 to 50% by weight of a substantially anhydrous, non-pigmented, polyhydric alcohol internal phase having surface tension properties which facilitate the preferential wetting of the ink repellent areas, the polyhydric alcohol internal phase comprising at least two polyhydric alcohols having from 2 to 5 carbon atoms, to thereby apply ink to the ink-receptive, image areas and polyhydric alcohol to the ink-repellent, non-image areas, (b) transferring the inked image from the plate to an ink receptive material, and (c) repeating the inking and printing steps of (a) and (b) without intermediate application of dampening solution to the printing plate.

18. An ink emulsion as claimed in claim 1 substantially as hereinbefore described in any one of examples 1 to 10 and 16 to 25 excluding the comparative tests.

19. A process of lithographic printing as claimed in claim 17 substantially as hereinbefore described in any one of examples 11 to 15.

20. A process of lithographic printing which comprises (a) contacting a lithographic printing plate possessing an image defined by ink receptive and ink-repellent areas with an emulsion as claimed in any one of claims 1 to 16 and 18, (b) transferring the inked image from the plate to an ink receptive material, and (c) repeating the inking and printing steps of (a) and (b) without intermediate application of dampening solution to the printing plate.

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